PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 02 November 2000 (02.11.00)	
International application No. PCT/EP00/02890	**Applicant's or agent's file reference** 06470.0
International filing date (day/month/year) 31 March 2000 (31.03.00)	**Priority date** (day/month/year) 31 March 1999 (31.03.99)
Applicant LEMMER, Oliver et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

07 October 2000 (07.10.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland** Facsimile No.: (41-22) 740.14.35	Authorized officer Pascal Piriou Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION TREATY

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INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 06470.0	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/EP 00/02890	International filing date *(day/month/year)* 31/03/2000	(Earliest) Priority Date *(day/month/year)* 31/03/1999
Applicant CEMECON-CERAMIC METAL COATINGS...		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

[ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

[ ] contained in the international application in written form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readble form.

[ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

[X] the text is approved as submitted by the applicant.

[ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

[X] the text is approved as submitted by the applicant.

[ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ______

[ ] as suggested by the applicant.

[ ] because the applicant failed to suggest a figure.

[ ] because this figure better characterizes the invention.

[X] None of the figures.

INTERNATIONALER [redacted]HERCHENBERICHT

Internationales Aktenzeichen:
PCT[redacted]00/02890

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
C23C28/04,B23B27/20

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK 7

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
B23B,B23Q,C04B,C23C

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	EP 0596619 A (CRYSTALLUME) 11 May 1994, the whole document. --	1-15
A	DATABASE WPI Week 199310 Derwent Publications Ltd., London, GB; Class B23B, AN 1993-079840 & JP 05 023903 A (MITSUBISHI MATERIALS CORP.) 02 February 1993, abstract. --	1-15
A	DATABASE WPI Week 199239 Derwent Publications Ltd., London, GB; Class B23B,	1-15

☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

☒ Siehe Anhang Patentfamilie

* Besondere Kategorien von angegebenen Veröffentlichungen:

"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist

"E" älteres Dokument das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist.

"L" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)

"O" Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht

"P" Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist

"T" Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist.

"X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann allein aufgrund dieser Veröffentlichung nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden

"Y" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist

"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts
19 Juni 2000	01.09.00

Name und Postanschrift der Internationalen Recherchenbehörde	Bevollmächtigter Bediensteter
Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	BECK

Internationales Akte[illegible]n PCT/EP 00/02890

III. EINSCHLÄGIGE VERÖFFENTLICHUNGEN (Fortsetzung von Blatt 2)		
Art *	Kennzeichnung der Veröffentlichung, soweit erforderlich unter Angabe der maßgeblichen Teile	Betr. Anspruch Nr.
	AN 1992-319863 & JP 04 223806 A (MITSUBISHI MATERIALS CORP.) 13 August 1992, abstract. ----	

ANHANG

Zum internationalen Recherchen richt über die internationale Pate anmeldung Nr.

ANNEX

To the International Search Report to the international Patent Application No.

ANNEXE

Au rapport de recherche international relativ à la demande de brevet international n°

PCT/EP 00/02890 SAE 278731

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This annex lists the patent family members relating to the patent documents cited in the above-mentioned search report. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

La presénte annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l' Office.

Im Recherchenbericht angeführte Patentdokumente Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
EP A1 596619	11-05-1994	CA AA 2102159	04-05-1994
		JP A2 6316764	15-11-1994
JP A2 5023903	02-02-1993	none	
JP A2 4223806	13-08-1992	none	

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TENT COOPERATION TR[illegible]Y

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REC'D 3 0 MAY 2001
WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 06470.0	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP00/02890	International filing date *(day/month/year)* 31/03/2000	Priority date *(day/month/year)* 31/03/1999

International Patent Classification (IPC) or national classification and IPC
C23C28/04

Applicant
CEMECON-CERAMIC METAL COATINGS...

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 7 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 12 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand 07/10/2000	Date of completion of this report 28.05.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Teppo, K-M Telephone No. +49 89 2399 8130

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP00/02890

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, pages:

1,2,5,6,11-15,17, 18	as originally filed			
3,3a,4,7-10,16, 16a	as received on	16/03/2001	with letter of	14/03/2001

Claims, No.:

4 (part),5-13	as received on	16/03/2001	with letter of	14/03/2001
1-3,4 (part)	as received on	15/05/2001	with letter of	14/05/2001

Drawings, sheets:

1/4-4/4	as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence

listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:
   ☐ the claims, Nos.:
   ☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)
   see separate sheet

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

   ☐ the entire international application.

   ☐ claims Nos. .

because:

   ☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

   ☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

   ☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

   ☒ no international search report has been established for the said claims Nos. 9, 10.

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

   ☐ the written form has not been furnished or does not comply with the standard.

   ☐ the computer readable form has not been furnished or does not comply with the standard.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-8
	No:	Claims	11-13
Inventive step (IS)	Yes:	Claims	1-8
	No:	Claims	11-13
Industrial applicability (IA)	Yes:	Claims	1-13
	No:	Claims	

2. Citations and explanations
   see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item I
Basis of the report

Amendments added to p. 16, l.17-25 submitted with the letter of 14.3.2001 include subject-matter that goes beyond the disclosure of the international application as filed (Art. 34(2)(b) PCT). This is due to the fact, that replacing process conditions of table 2 with those of D2 to produce a nano-crystalline diamond in the second carbon layer of the current application is a novel combination. Moreover, D2 defines only 2 parameters of the 10 parameters required in table 2 of the present application. Thus, this report is based on the originally submitted p. 16. Hence, p. 16a becomes futile.

Re Item V
Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. CITED DOCUMENTS

Reference is made to the following document:

D1: EP 0 596 619 A (CRYSTALLUME) 11 May 1994
D2: D. M. GRUEN: 'Nucleation, Growth and Micro-structure of Nano-Crystalline Diamond Films', MRS-BULLETIN-PUBLICATION OF THE MATERIALS RESEARCH SOCIETY, vol. 23, no. 9, pages 32 to 35, cited in the application.

2. NOVELTY, Art. 33(1) and (2) PCT

2.1
Document D1 discloses a diamond-coated tool suitable for machining and cutting having a substrate and two carbon layers of diamond crystal structure (see D1, col. 1, l. 1-17 and fig. 1, col. 4, l. 14-16). The substrate material being e.g. tungsten carbide (col. 4, l. 16-17). When the first carbon layer (CL1) is deposited, the amount of the carbon carrier gas (CH_4) is 1 vol-% (see D1, fig. 5, col. 9, l. 21-24) and when the second carbon layer (CL2) is deposited, the amount of the carbon carrier gas (CH_4) is 5 vol-% (see D1, fig. 5, col. 9, l. 26-27).

The thermal expansion coefficient of CL1 (αt1) is implicitly smaller than that of the WC-substrate (αts) even though exact values are not disclosed, since this is the case also in the application, where the same materials are used.
The fraction of the carbon with a diamond structure in CL1 (fC1) is lower than in CL2, because to manufacture CL2 the amount of CH_4 is raised and this is known to diminish the amount of carbon with diamond structure (see D1 col. 9, l. 26 and the description p. 9, l. 16-24).
Due to the fact that the fraction of carbon with a diamond structure in CL2 (fC2) is smaller than in CL1 the thermal coefficient of CL2 (αt2) is increased by contrast to CL1 (see the description p. 4, l. 14-26). Both of the layers (A) and (B) are considered to contain "highly predominant" fractions of carbon.

Therefore the subject-matter of claims 11 and 13 is not considered to be novel.

2.2
The subject-matter of the independent product claim 1 and the subject-matter of the claims dependent on it i.e. claims 2-10 are regarded as novel over the prior art, due to the fact that the second carbon layer claimed in claim 1 includes nano-crystalline diamond. This is not disclosed in any of the relevant prior art documents.

3. INVENTIVE STEP, Art. 33(1) and (3) PCT

The problem to be solved by the present invention may be regarded as how to provide diamond-coated tool with reduced instances of chipping. The applicant achieves this by applying a second carbon layer onto the first one, the second layer comprising a smaller fraction of carbon with a diamond carbon structure and most of all nano-crystalline diamond. Nano-crystalline diamond increases the thermal extension coefficient of the second carbon layer and thus reduces the risk of chipping. Hence, the inventiveness of the subject-matter of claims 1-10 is assured.

The wording of claim 11 does not include producing nano-crystalline carbon and thus, the subject-matter of claim 11 is regarded as well as not novel also obvious as it does not resolve the problem posed.

Moreover, the process conditions used during the deposition of CL1 in D1 are obviously chosen to achieve as high as possible fraction of carbon with diamond structure. Therefore the subject-matter of claim 12 lacks an inventive step.

Re Item VII
Certain defects in the international application

(a) The term **"crystalline"** is written without the letter "h".

Re Item VIII
Certain observations on the international application

The term "highly predominant" used in claims 1 and 11 is vague and unclear and leaves the reader in doubt as to the meaning of the technical feature to which it refers. Should the aforementioned vaguely defined technical feature be interpreted as a special technical feature for the assessment of novelty or inventive step, the definitions of said claims are considered to lack clarity (Art. 6 PCT).

bit is formed by a carbon layer with a lower diamond fraction return substantially poorer results by comparison with the inverted layer sequence.

EP 0 596 619 A1 describes a diamond-coated article with integral wear-out-indicator. Two diamond layers are provided differing in their electrical or optical characteristics in order to provide a means for indicating the wear-out of the diamond coating. The process conditions disclosed indicate that the diamond layers are of conventional columnar structure.

Starting herefrom, it is the object of the invention to create a coated tool having a substrate and a carbon layer, applied to the substrate, with carbon in a diamond crystal structure, in the case of which tool the risk of instances of chipping of the carbon layer are effectively reduced. Moreover, the aim is also to specify a process for producing such a tool.

The object is achieved by means of a tool having the features of Claim 1. In context with the invention, the expression "tool" includes each component having a coating serving for abrasion resistance of the component. Examples of such a tool are cutting tools like mills, drills, twist drills, reamers, threaders, grinding tools, trueing tools and honing tools, forming / shaping tools like drawing tools, stamping tools and punching tools, and components of the above-mentioned kind like wear parts, fairlead bushes, lands, guide surfaces, slide faces, slide bearings and cutting faces. The most prominent examples are guide surfaces of twist drills, guide surfaces of reamers and cutting surfaces of inserts. The last-mentioned examples refer to the fact that in most tools the cutting components are combined with sliding surfaces defining the position of the blade, such that compo-

nents are integral with the tool. In this connection, the smooth diamond layers are particularly advantageous, because they have a high hardness and a low coefficient of friction. The components may be mounted to a tool or made up by certain tool surfaces. In many cases, the tool coating includes a tool egde.

The fraction of carbon with a diamond crystal structure is preferably very high in the first carbon layer, for example in accordance with previously used diamond coatings in the case of tools for machining workpieces. It has surprisingly been established that in the case when, by contrast with the first carbon layer, the second carbon layer has a smaller fraction of carbon with a diamond crystal structure, the formation of cracks in the carbon layer can be effectively reduced overall, with the result that instances of chipping occur very much more rarely.

In principle, both the first and the second carbon layer contain a highly predominant carbon fraction in diamond crystal structure (80-100%). These layers are mostly denoted in the literature as diamond layers. The remaining carbon is graphite or amorphous phases.

It is conjectured that the different coefficients of thermal expansion of the first and second carbon layers contribute to a reduction in the formation of cracks. Since, by contrast with the first carbon layer, the fractions of carbon with a graphite crystal structure and amorphous structure are increased in the second carbon layer, the coefficient of thermal expansion is also increased by contrast with the first carbon layer. The second carbon layer includes or consists of nano-crystalline diamond typically being surrounded by carbon of non-diamond structure. The last-mentioned carbon serves to increase the thermal extension coefficient of the second carbon layer. The generation of nano-crystalline diamond films on substrates is, e.g. described in "Nucleation, Growth and Microstructure of Nanocrystalline Diamond Films" in "MRS Bulletin-Publication of the Materials Research Society", September 1998, Vol. 23, No. 9, p. 32-35, of Dieter M. Gruen.

1 to 40 μm, the value ranges of 4 to 20 μm and 6 to 15 μm respectively leading to increasingly better results for the adhesive strength of the carbon layers.

The first carbon layer preferably has a structure such that upon irradiation by laser light at a wavelength of 514 nm (emission line of the Ar ion laser) the first carbon layer generates a Raman spectrum in the case of which, after subtraction of a signal background, the intensity ratio K_A of a peak S, representative of carbon with a diamond crystal structure, at 1332 cm^{-1} to a peak F, representative of carbon lacking a diamond crystal structure, at 1560 cm^{-1} is in the range of from ∞ to 0.5, in which case $K_A = I(S_A)/I(F_A)$ is the diamond value for the first carbon layer.

The intensity ratio K_A of the peak S, representative of carbon with a diamond crystal structure, at 1332 cm^{-1} to the peak F, representative of carbon lacking a diamond crystal structure, at 1560 cm^{-1} is, further, preferably in the range of from 10 to 1.0 which, for the ratio of the fractions of carbon with a diamond crystal structure to carbon of a different, for example graphitic or amorphous structure, has proved to be particularly favourable for the first carbon layer.

The second carbon layer preferably has a structure such that upon irradiation by laser light at a wavelength of 514 nm the second carbon layer generates a Raman spectrum in the case of which, after subtraction of a signal background, the intensity ratio K_B of a peak S, representative of carbon with

a diamond crystal structure, at 1332 cm^{-1} to the peak F, representative of carbon lacking a diamond crystal structure, at 1560 cm^{-1} is in the range of from 2 to 0, in which case $K_B = I(S_A)/I(F_A)$ is the diamond value for the second carbon layer.

The intensity ratio K_B of the peak S, representative of carbon with a diamond crystal structure, at 1332 cm^{-1} to the peak F, representative of carbon lacking a diamond crystal structure, at 1560 cm^{-1} is, further, preferably in the range of from 1 to 0.1.

The secondary condition applies to all the abovenamed data on ranges in that the fraction of carbon with a diamond crystal structure in the second carbon layer is lower than the fraction of carbon with a crystal diamond structure in the first carbon layer, that is to say $K_A > K_B$. It is also possible in principle that in the case of the first carbon layer the peak F, and in the case of the second carbon layer the peak S is respectively completely missing in the Raman spectrum.

The second carbon layer preferably has a minimum thickness of 0.5 μm, something which marks it off from effects which occur at the end of a conventional CVD diamond coating process and in the case of which a structure lacking diamonds can occur which cannot be denoted as a layer in the sense of this description and comprises a few layers of atoms. What is decisive, however, is that the thickness of the second carbon layer is selected in such a way that there is an adhesivity of the layers on the substrate which is markedly increased by contrast with the first carbon layer alone.

A method for producing a tool substrate coated with carbon in accordance with Claim 9 is likewise the subject matter

of the invention.

The essential process parameters for applying carbon layers with a high fraction of carbon in a diamond crystal structure are known. These include the feeding of a carbon carrier gas such as methane, and the feeding of molecular hydrogen, the setting of a suitable substrate temperature and the coating period over which, first and foremost, the thickness of the carbon layers is set.

The process conditions for applying the first carbon layer for a fraction of carbon with a diamond crystal structure which is as high as possible are preferably optimized in step a). This produces the known diamond coatings for components which exhibit excellent wear resistance.

In step b), the process conditions of step a) are preferably changed in order to reduce the fraction of carbon with a diamond crystal structure by contrast with the first layer.

The invention is explained by way of example in yet more detail below with the aid of the figures, in which:

Figure 1 shows a diagrammatic cross sectional view of a section of a coated component;

Figure 2 shows an exemplary Raman spectrum illustrating the diamond value;

Figure 3 shows a Raman spectrum of the first carbon layer of the component of Figure 1;

Figure 4 shows a Raman spectrum of the second layer of the component of Figure 1;

Figure 5 shows an electron microscope image of a cross section, produced by means of a fracture, of an edge in the case of the component of Figure 1 at an approximately 1,500-fold magnification;

Figure 6 shows a detail from Figure 5 at an approximately 6,500-fold magnification; and

Figure 7 shows an electron microscope image of the outer

longwave sides of the peak S. The height of the peak S is yielded from the difference between the intensity values for the peak maximum in the region of the wavenumber 1332 cm^{-1} and the intensity of the background for the same wavenumber, a straight line which connects the points P1 and P2 being used to estimate the intensity of the background.

Similarly, the background for the peak F is yielded from a straight line connecting the point P2 and a point P3 which are arranged on the shortwave side of the peak F.

Further peaks can also occur in special cases, but they are not relevant if they are outside the wavenumber interval of 1200-1700 cm^{-1}, or their magnitude is less than the peak height of the peaks S and F. For example, at 1150 cm^{-1}, in certain instances a peak can be observed which is to be ascribed to nano-crystalline diamonds. The occurrence of this peak in a Raman-spectrum depends on the amount of nano-crystalline diamond. For producing nano-crystalline diamond in the second carbon layer the process conditions of table 2 have to be replaced by process conditions as described in "Nucleation, Growth and Microstructure of Nanocrystalline Diamond Films" published in "MRS Bulletin-Publication of the Materials Research Society", September 1998, vol. 23, no. 9, p. 32-35, of Dieter M. Gruen. Nano-crystalline diamond is surrounded by carbon of non-diamond structure. Therefore, the presence of nano-crystalline diamond in the second carbon layer is advantagous because the carbon with non-diamond structure around the nano-crystalline diamonds increases the thermal expension coefficient of the second carbon layer.

A peak occurring at 1355 cm^{-1} (so-called D-band) is likewise Raman scattered light which is, however, generated by violating the selection rules for the Raman scattering on the basis of increased focal surface scattering. The D-band is

greatly widened and is eliminated by the background correction described above.

The diamond value K_A or K_B serves for identifying the first and the second carbon layer, and is associated with the actual diamond fraction only to the extent that there is a strict monotonic dependence in the mathematical sense.

Claims

1. Coated tool, in particular for machining, having a substrate, which has a predetermined coefficient of thermal expansion, a first carbon layer which is deposited on the substrate, which has a predetermined highly predominant fraction of carbon with a diamond crystal structure and a coefficient of thermal expansion which is smaller than the coefficient of thermal expansion of the substrate and at least one second carbon layer (B), which is deposited further outside with reference to the substrate (M) than the first carbon layer (A), and in the case of which the fraction of carbon with a diamond crystal structure is highly predominant but lower than the predetermined fraction of carbon with a crystal diamond structure in the first carbon layer (A), and in the case of which the coefficient of thermal expansion is greater than the coefficient of thermal expansion of the first carbon layer (A), characterized in that the second carbon layer includes nano-crystalline diamond.

2. Tool according to Claim 1, characterized in that the second carbon layer (B) consists of nano-crystalline diamond.

3. Tool according to Claim 1 or 2, characterized in that the second carbon layer (B) is deposited directly on the first carbon layer (A).

4. Tool according to Claim 1 or 2, characterized in that formed between the first carbon layer (A) and the second carbon layer (B) is an interlayer in the case of which the fraction of carbon with a diamond crystal structure drops continuously from the first carbon

layer (A) in the direction of the second carbon layer (B).

5. Tool according to one of Claims 1 to 4, characterized in that it has an overall thickness of the first carbon layer (A) and the second carbon layer (B) in the range from 1 to 40 μm.

6. Tool according to Claim 5, characterized in that it has an overall thickness of the first carbon layer (A) and the second carbon layer (B) in the range of 4 to 20 μm.

7. Tool according to Claim 6, characterized in that an overall thickness of the first carbon layer (A) and of the second carbon layer (B) in the range of 6 to 15 μm is formed.

8. Tool according to one of Claims 1 to 7, characterized in that the second carbon layer (B) has a minimum thickness of 0.5 μm.

9. Tool according to one of Claims 8, characterized in that further material layers are arranged between the first carbon layer and the second carbon layer.

10. Tool according to one of Claims 1 to 9, characterized in that with reference to the substrate beyond the second carbon layer further material layers are arranged.

11. Process for producing a tool substrate which is coated with carbon and has a predetermined coefficient of thermal expansion, having the following steps:

a) depositing onto the tool substrate (M) a first

carbon layer (A), the process conditions being selected such that the carbon layer (A) contains a predetermined highly predominant fraction of carbon with a diamond crystal structure and has a smaller coefficient of thermal expansion than the tool substrate (M); and

b) depositing a second carbon layer (B), which lies further outside with reference to the substrate (M) than the first carbon layer (A), the process conditions being selected in such a way that by contrast with the predetermined fraction of carbon with a diamond crystal structure of the first carbon layer (A) the second carbon layer (B) has a highly predominant but reduced proportion of carbon with a diamond crystal structure and a larger coefficient of thermal expansion than the first carbon layer (A).

12. Process according to Claim 10, in which in step a) the process conditions are selected such that the first carbon layer (A) has a high as possible a fraction of carbon with diamond crystal structure.

13. Process according to Claim 11 or 12, in which in step b) the process conditions of step a) are changed to reduce the fraction of carbon with a diamond crystal structure by comparison with the first carbon layer (A).

bit is formed by a carbon layer with a lower diamond fraction return substantially poorer results by comparison with the inverted layer sequence.

Starting herefrom, it is the object of the invention to create a coated tool having a substrate and a carbon layer, applied to the substrate, with carbon in a diamond crystal structure, in the case of which tool the risk of instances of chipping of the carbon layer are effectively reduced. Moreover, the aim is also to specify a process for producing such a tool.

The object is achieved by means of a tool having the features of Claim 1. In context with the invention, the expression "tool" includes each component having a coating serving for abrasion resistance of the component. Examples of such a tool are cutting tools like mills, drills, twist drills, reamers, threaders, grinding tools, trueing tools and honing tools, forming / shaping tools like drawing tools, stamping tools and punching tools, and components of the above-mentioned kind like wear parts, fairlead bushes, lands, guide surfaces, slide faces, slide bearings and cutting faces. The most prominent examples are guide surfaces of twist drills, guide surfaces of reamers and cutting surfaces of inserts. The last-mentioned examples refer to the fact that in most tools the cutting components are combined with sliding surfaces defining the position of the blade, such that components are integral with the tool. In this connection, the smooth diamond layers are particularly advantageous, because they have a high hardness and a low coefficient of friction. The components may be mounted to a tool or made up by certain tool surfaces. In many cases, the tool coating includes a tool egde.

The fraction of carbon with a diamond crystal structure is preferably very high in the first carbon layer, for example in accordance with previously used diamond coatings in the case of tools for machining workpieces. It has surprisingly been established that in the case when, by contrast with the first carbon layer, the second carbon layer has a smaller fraction of carbon with a diamond crystal structure, the formation of cracks in the carbon layer can be effectively reduced overall, with the result that instances of chipping occur very much more rarely.

In principle, both the first and the second carbon layer contain a highly predominant carbon fraction in diamond crystal structure (80-100%). These layers are mostly denoted in the literature as diamond layers. The remaining carbon is graphite or amorphous phases.

It is conjectured that the different coefficients of thermal expansion of the first and second carbon layers contribute to a reduction in the formation of cracks. Since, by contrast with the first carbon layer, the fractions of carbon with a graphite crystal structure and amorphous structure are increased in the second carbon layer, the coefficient of thermal expansion is also increased by contrast with the first carbon layer. The second carbon layer can include or consist of nano-chrystalline diamond typically being surrounded by carbon of non-diamond structure. The last-mentioned carbon serves to increase the thermal extension coefficient of the second carbon layer. The generation of nano-chrystalline diamond films on substrates is, e.g. described in "Nucleation, Growth and Micro-Structure of Nano-Chrystalline Diamond Films" in "MRS Bulletin-Publication of the Materials Research Society", September 1998, Vol. 23, No. 9, p. 32-33, of Dieter M. Gruen. The contents of this citation is incorporated herein by reference.

1 to 40 μm, the value ranges of 4 to 20 μm and 6 to 15 μm respectively leading to increasingly better results for the adhesive strength of the carbon layers.

The ratio of the thickness of the first carbon layer to the thickness of the second carbon layer can be in the range of 0.05 to 0.9, while a range of from 0.1 to 0.5 is to be regarded as preferred for this ratio.

The first carbon layer preferably has a structure such that upon irradiation by laser light at a wavelength of 514 nm (emission line of the Ar ion laser) the first carbon layer generates a Raman spectrum in the case of which, after subtraction of a signal background, the intensity ratio K_A of a peak S, representative of carbon with a diamond crystal structure, at 1332 cm^{-1} to a peak F, representative of carbon lacking a diamond crystal structure, at 1560 cm^{-1} is in the range of from ∞ to 0.5, in which case $K_A = I(S_A)/I(F_A)$ is the diamond value for the first carbon layer.

The intensity ratio K_A of the peak S, representative of carbon with a diamond crystal structure, at 1332 cm^{-1} to the peak F, representative of carbon lacking a diamond crystal structure, at 1560 cm^{-1} is, further, preferably in the range of from 10 to 1.0 which, for the ratio of the fractions of carbon with a diamond crystal structure to carbon of a different, for example graphitic or amorphous structure, has proved to be particularly favourable for the first carbon layer.

The second carbon layer preferably has a structure such that upon irradiation by laser light at a wavelength of 514 nm the second carbon layer generates a Raman spectrum in the case of which, after subtraction of a signal background, the intensity ratio K_B of a peak S, representative of carbon with

a diamond crystal structure, at 1332 cm^{-1} to the peak F, representative of carbon lacking a diamond crystal structure, at 1560 cm^{-1} is in the range of from 2 to 0, in which case $K_B = I(S_A)/I(F_A)$ is the diamond value for the second carbon layer.

The intensity ratio K_B of the peak S, representative of carbon with a diamond crystal structure, at 1332 cm^{-1} to the peak F, representative of carbon lacking a diamond crystal structure, at 1560 cm^{-1} is, further, preferably in the range of from 1 to 0.1.

The secondary condition applies to all the abovenamed data on ranges in that the fraction of carbon with a diamond crystal structure in the second carbon layer is lower than the fraction of carbon with a crystal diamond structure in the first carbon layer, that is to say $K_A > K_B$. It is also possible in principle that in the case of the first carbon layer the peak F, and in the case of the second carbon layer the peak S is respectively completely missing in the Raman spectrum.

The second carbon layer preferably has a minimum thickness of 0.5 μm, something which marks it off from effects which occur at the end of a conventional CVD diamond coating process and in the case of which a structure lacking diamonds can occur which cannot be denoted as a layer in the sense of this description and comprises a few layers of atoms. What is decisive, however, is that the thickness of the second carbon layer is selected in such a way that there is an adhesivity of the layers on the substrate which is markedly increased by contrast with the first carbon layer alone.

A method for producing a tool substrate coated with carbon in accordance with Claim 10 is likewise the subject matter

of the invention.

The essential process parameters for applying carbon layers with a high fraction of carbon in a diamond crystal structure are known. These include the feeding of a carbon carrier gas such as methane, and the feeding of molecular hydrogen, the setting of a suitable substrate temperature and the coating period over which, first and foremost, the thickness of the carbon layers is set.

The process conditions for applying the first carbon layer for a fraction of carbon with a diamond crystal structure which is as high as possible are preferably optimized in step a). This produces the known diamond coatings for components which exhibit excellent wear resistance.

In step b), the process conditions of step a) are preferably changed in order to reduce the fraction of carbon with a diamond crystal structure by contrast with the first layer. This can advantageously be performed by reducing the substrate temperature in step b) by comparison with step a). Moreover, in step b) the fraction of the carbon carrier gas used can also be increased by contrast with step a), as a result of which the conditions for producing a carbon layer with a high fraction of carbon with a diamond crystal structure are "worsened".

The two measures named for changing the process conditions from step a) to step b) can be taken individually or else in combination with one another.

In the case of the CVD process used, in particular the hot-filament CVD process, it is also possible in step b) as contrasted with step a) to increase the distance of the substrate from the gas excitation, or to reduce the supply

of power for the gas excitation. The introduction of extraneous gases likewise leads in most cases to a reduction in the fraction of carbon with a diamond crystal structure. An exception is formed by oxidizing gases which can also lead to an increase in diamond, and can thus be used to support the production of the first carbon layer. The flow of the process gases, and the pressure in the coating facility can also be set to differ from their ideal values, which are typically present in step a), in order to achieve the process conditions for step b).

The invention is explained by way of example in yet more detail below with the aid of the figures, in which:

Figure 1 shows a diagrammatic cross sectional view of a section of a coated component;

Figure 2 shows an exemplary Raman spectrum illustrating the diamond value;

Figure 3 shows a Raman spectrum of the first carbon layer of the component of Figure 1;

Figure 4 shows a Raman spectrum of the second layer of the component of Figure 1;

Figure 5 shows an electron microscope image of a cross section, produced by means of a fracture, of an edge in the case of the component of Figure 1 at an approximately 1,500-fold magnification;

Figure 6 shows a detail from Figure 5 at an approximately 6,500-fold magnification; and

Figure 7 shows an electron microscope image of the outer

longwave sides of the peak S. The height of the peak S is yielded from the difference between the intensity values for the peak maximum in the region of the wavenumber 1332 cm^{-1} and the intensity of the background for the same wavenumber, a straight line which connects the points P1 and P2 being used to estimate the intensity of the background.

Similarly, the background for the peak F is yielded from a straight line connecting the point P2 and a point P3 which are arranged on the shortwave side of the peak F.

Further peaks can also occur in special cases, but they are not relevant if they are outside the wavenumber interval of 1200-1700 cm^{-1}, or their magnitude is less than the peak height of the peaks S and F. For example, at 1150 cm^{-1}, in certain instances a peak can be observed which is to be ascribed to nano-crystalline diamonds. Nano-chrystalline diamond is surrounded by carbon of non-diamond structure. Therefore, the presence of nano-chrystalline diamond in the second carbon layer is advantagous because the carbon with non-diamond structure around the nano-chrystalline diamonds increases the thermal expension coefficient of the second carbon layer.

A peak occurring at 1355 cm^{-1} (so-called D-band) is likewise Raman scattered light which is, however, generated by violating the selection rules for the Raman scattering on the basis of increased focal surface scattering. The D-band is greatly widened and is eliminated by the background correction described above.

The diamond value K_A or K_B serves for identifying the first and the second carbon layer, and is associated with the actual diamond fraction only to the extent that there is a strict monotonic dependence in the mathematical sense.

Claims

1. Coated tool, in particular for machining, having a substrate, which has a predetermined coefficient of thermal expansion, and a first carbon layer which is deposited on the substrate, which has a predetermined fraction of carbon with a diamond crystal structure and a coefficient of thermal expansion which is smaller than the coefficient of thermal expansion of the substrate, characterized in that provision is made of at least one second carbon layer (B), which is deposited further outside with reference to the substrate (M) than the first carbon layer (A), and in the case of which the fraction of carbon with a diamond crystal structure is lower than the predetermined fraction of carbon with a crystal diamond structure in the first carbon layer (A), and in the case of which the coefficient of thermal expansion is greater than the coefficient of thermal expansion of the first carbon layer (A).

2. Tool according to Claim 1, characterized in that the second carbon layer (B) is deposited directly on the first carbon layer (A).

3. Tool according to Claim 1, characterized in that formed between the first carbon layer (A) and the second carbon layer (B) is an interlayer in the case of which the fraction of carbon with a diamond crystal structure drops continuously from the first carbon layer (A) in the direction of the second carbon layer (B).

4. Tool according to one of Claims 1 to 3, characterized in that it has an overall thickness of the first carbon layer (A) and the second carbon layer (B) in the range

from 1 to 40 μm.

5. Tool according to Claim 4, characterized in that it has an overall thickness of the first carbon layer (A) and the second carbon layer (B) in the range of 4 to 20 μm.

6. Tool according to Claim 5, characterized in that an overall thickness of the first carbon layer (A) and of the second carbon layer (B) in the range of 6 to 15 μm is formed.

7. Tool according to one of Claims 1 to 6, characterized in that the ratio of the thickness of the first carbon layer (A) to the thickness of the second carbon layer (B) is in the range of 0.05 to 0.9.

8. Tool according to Claim 7, characterized in that the ratio of the thickness of the first carbon layer (A) to the thickness of the second carbon layer (B) is in the range of 0.1 to 0.5.

9. Tool according to one of Claims 1 to 8, characterized in that the second carbon layer (B) has a minimum thickness of 0.5 μm.

10. Tool according to one of claims 1 to 9, characterized in that the second carbon layer (B) consists of nano-chrystalline diamond.

11. Process for producing a tool substrate which is coated with carbon and has a predetermined coefficient of thermal expansion, having the following steps:

a) depositing onto the tool substrate (M) a first carbon layer (A), the process conditions being

selected such that the carbon layer (A) contains a predetermined fraction of carbon with a diamond crystal structure and has a smaller coefficient of thermal expansion than the tool substrate (M); and

b) depositing a second carbon layer (B), which lies further outside with reference to the substrate (M) than the first carbon layer (A), the process conditions being selected in such a way that by contrast with the predetermined fraction of carbon with a diamond crystal structure of the first carbon layer (A) the second carbon layer (B) has a reduced proportion of carbon with a diamond crystal structure and a larger coefficient of thermal expansion than the first carbon layer (A).

12. Process according to Claim 11, in which in step a) the process conditions are selected such that the first carbon layer (A) has a high as possible a fraction of carbon with diamond crystal structure.

13. Process according to Claim 11 or 12, in which in step b) the process conditions of step a) are changed to reduce the fraction of carbon with a diamond crystal structure by comparison with the first carbon layer (A).

14. Process according to Claim 13, in which in step b) the substrate temperature is reduced by comparison with step a).

15. Process according to one of Claims 13 or 14, in which in step b) the proportion of carbon carrier gas used is increased by comparison with step a).